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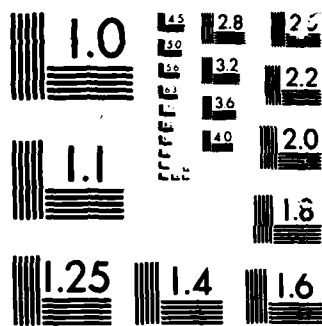
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# CHEMISTRY OF NON-EQUILIBRIUM FILM DEPOSITION

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June 30, 1981 through October 1, 1985

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Bolling AFB, DC 20332

P.H. Kobrin and A.B. Harker  
Principal Investigators

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## RESEARCH OBJECTIVES

The Science Center's four-year study of the processes involved in nonequilibrium thin-film chemistry has covered a range of photochemical- and physical-deposition systems. The original activity focused on describing the mechanisms of photo-assisted thermal deposition in which the sticking coefficients of atomic species were significantly enhanced through laser irradiation of the substrate surface. This later expanded to an investigation of the chemical and physical processes involved in reactive photochemical deposition of dielectric oxides and finally to a comparative study of the parameters controlling reactive energetic-beam deposition of dielectric oxides and nitrides. This final report outlines the work previously reported and gives a more detailed description of the efforts in fiscal year 1985.



## STATUS OF RESEARCH EFFORT

### A. Laser Desorption from Nonabsorbing Surfaces

The initial efforts in studying the low-temperature laser-assisted deposition of atomic species led to a determination that the controlling process was the photo-induced desorption of surface contaminant species which were occupying the low-energy surface adsorption sites.<sup>1</sup> In order to study the controlling processes of this phenomena, an ultra-high vacuum apparatus equipped with a quadrupole mass spectrometer was developed to analyze species desorbed from optically transparent substrates by radiation from several pulsed laser sources. These experiments showed that omnipresent hydrocarbon contamination can be removed by ultraviolet light at 248 and 308 nm through a single-photon process while visible radiation at 458 nm desorbes the contaminants through a two-photon mechanism.<sup>2</sup> The desorption process involves only the breaking of the molecule-surface bond, not the photofragmentation of the adsorbed species. Temperature dependence studies indicated that the contaminant molecules are physisorbed rather than chemisorbed to quartz surfaces and are desorbed with slower than room-temperature velocities, if a Boltzmann distribution is assumed.<sup>3</sup>

### B. Photochemical Deposition

The photo-assisted desorption studies were extended to examine the mechanisms involved in the photochemical deposition of optical thin films. Thin films of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  were deposited photochemically using a variety of radiation sources. The resulting films were analyzed for chemical composition, stoichiometry, adhesion and hardness. The initial photochemical films lacked the stoichiometry, optical quality, and mechanical properties of thermally evaporated coatings.<sup>2</sup> Further refinements were made in which  $\text{TiO}_2$  was deposited by photolysis of gas-phase titanium isopropoxide.<sup>3</sup> When depos-





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ited on substrates heated to 120°C in the presence of an oxidizer, such as  $O_2$  or  $N_2O$ , the films approached the correct stoichiometry and did not contain the carbonyl contamination ubiquitous to the earlier photochemical experiments. Using titanium tetrachloride as a starting reagent yielded films with Cl contamination at the 2% level as determined using surface analysis techniques.<sup>4</sup> Photochemical deposition using tetramethyl tin, without an oxidizer, resulted in deposition of a metallic Sn film which was also contaminated with carbon species. The range of reactive radical and atomic species present in photochemical systems makes the suppression of contaminants difficult under low substrate temperature deposition conditions. Using a heated substrate, which encourages complete reaction of organometallics to oxides, produces higher quality films, but moves more into the regime of near-equilibrium thermal deposition. Hence, further efforts shifted to the study of the controlling processes in nonequilibrium energetic-beam deposition.

#### C. Nonequilibrium Physical Deposition

In fiscal years 1984 and 1985, a number of investigations of the phenomena controlling the structure and chemistry of energetically deposited films on unheated substrates were conducted using both single- and dual-reactive ion-beam deposition. The initial work was done with aluminum nitride and the oxides of titanium using Kaufman-type ion sources with metallic targets and reactive background gases. The experimental arrangement is shown in Figure 1. The system contains two Commonwealth Scientific ion sources, both with collimated 3 cm-diameter beams. The primary source (500-1500 eV) is directed onto the sputter target, while the lower-energy source (10-100 eV) is directed onto the deposition substrate. Both sources are equipped with neutralizing filaments to provide a degree of charge balance at the sputtered surface. The target and deposition substrate are arranged in nearly parallel planes to maximize the deposition flux at the surface.



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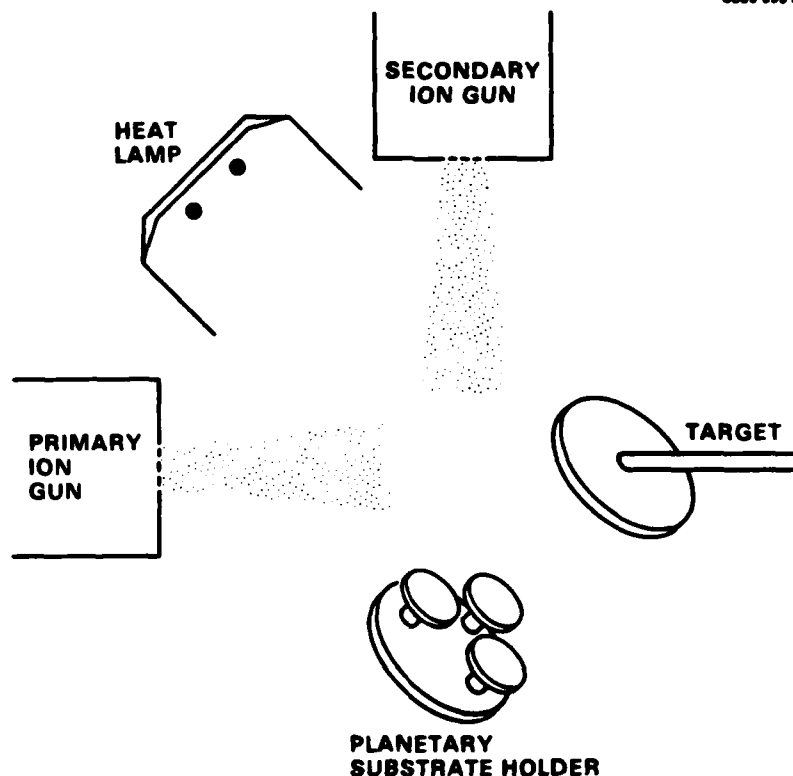


Fig. 1 Chamber geometry for single- and dual-beam deposition experiments.

The deposition chamber, designed and developed in this laboratory<sup>5</sup> is fully UHV compatible with all copper gasket seals and is pumped by two Balzer turbomolecular pumps (510 and 330 l/s). With bakeout, the base pressure in the chamber is  $3 \times 10^{-9}$  torr. Gases for the experiments were either Matheson research grade in 1 liter glass flasks or AirProducts pre-purified grade in steel cylinders. Gas compositions were routinely checked by a residual gas analyzer.

#### 1. Titanium Oxide Films

The titanium oxide films were initially studied for direct comparison with  $\text{TiO}_2$  films produced previously in the photochemical studies. The films were deposited from 99.7% purity metal targets using argon as the primary sputtering gas. Oxygen was added to the films by backfilling the chamber to



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$2 \times 10^{-5}$  torr. The  $O_2$  was not run through the Kaufman sources which extended the lifetimes of the filaments. Films were deposited on single-crystal silicon, glass slides, and cleaved single-crystal NaCl and KCl. The deposition experiments on the soluble salt substrates were carried out to provide samples for transmission electron microscope analysis and for a post-deposition annealing study of  $TiO_2$  carried out under a complimentary internal research project.<sup>6</sup>

The  $TiO_x$  films formed by single reactive ion-beam deposition were amorphous to the limit of analysis by x-ray and electron diffraction and routinely showed an oxygen deficiency as determined by x-ray photoelectron spectroscopy. Dual-beam films showed some fine polycrystalline structure. TEM analysis of the films, as floated from the NaCl and KCl substrates, showed that there is an inverse correlation between the magnitude of the measured refractive index and the distribution of extremely fine porosity in the films. Energy-dispersive x-ray (EDX) analysis confirmed that the included porosity contained Ar. Films with an index of 2.36 at 633 nm, prepared by dual ion-beam sputtering, showed a factor of 6 greater Ar content than single ion-beam deposited films with an index of 2.42.

The possibility of forming large-grained crystalline films by post-deposition annealing of amorphous  $TiO_2$  was investigated under IR&D sponsorship to determine if the two-dimensional restrictions placed upon grain development in very thin films could be used to enhance orientation and ordered grain growth, independent of substrate characteristics, to produce films with properties approaching those of a single crystal. Some of the significant observations from this study were:

1. The dominant factors in the crystallization were found to be the thickness and density of the films.
2. 100 nm-thick films annealed free-standing (on nickel grids) and those transformed on substrates showed essentially the same orientation



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behavior, indicating minimal substrate contributions to grain growth behavior. Films that had been grown on a rotating substrate and those that had been grown on a stationary substrate also showed similar annealing patterns.

3. Oriented large-grain development is controlled by the competition between individual grain nucleation and their subsequent growth. High temperatures lead to increased nucleation site formation and rapid transformation, while lower temperatures favor limited nucleation sites and hence the growth of large grains.

The effect of film thickness on crystallization is dramatic. Figure 2 shows a TEM micrograph of a 26 nm film annealed for 15 h at 500°C. Films of this thickness showed only very local transformation into submicron polycrystalline grains at 400°C, remaining primarily amorphous even at annealing times of 104 h. At 500°C, these films fully transformed into void separated submicron crystallites. Grain growth is limited by the formation of voids, as the density changes in the transforming material cannot be accommodated. The higher temperatures involved in the transformation lead to the formation of multiple crystalline phases including anatase, brookite, and rutile.

With increasing film thickness (> 30 nm), local transformation occurs, yielding well-formed ellipsoidal single crystallites of anatase with their a-axis normal to the substrate plane (Fig. 3). The individual crystallites, forming as islands in the amorphous film, grow together with longer annealing times.

At thicknesses of 90 to 160 nm, the films completely transform to anatase at temperatures above 370°C after only 4 h. The transformation produces {100} oriented anatase grains 5 to 20  $\mu\text{m}$  in length (Fig. 4). The nearly parallel step structure in some of the narrow grains is characteristic of the interfacial control of the growth mechanism, in which porosity regularly segregates to cellular boundaries. The degree of misorientation between the adjacent parallel grains is generally less than 2°.



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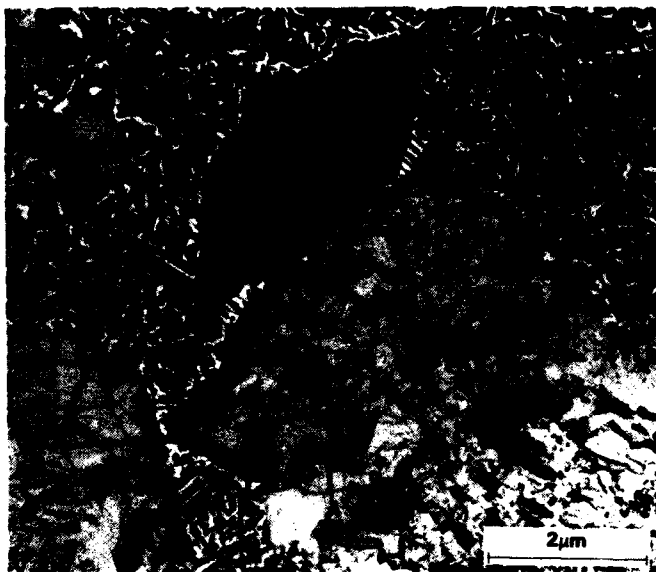


Fig. 2 TEM micrograph of void-limited grain growth in 26 nm TiO<sub>2</sub> film after annealing to 500°C for 15 hours. Needle-like grains are brookite, large grains anatase, and the smaller spherical particles rutile.

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Fig. 3 TEM micrograph of single-crystal <100> anatase forming in plane of 67 nm-thick TiO<sub>2</sub> film, after 15 hours at 400°C.



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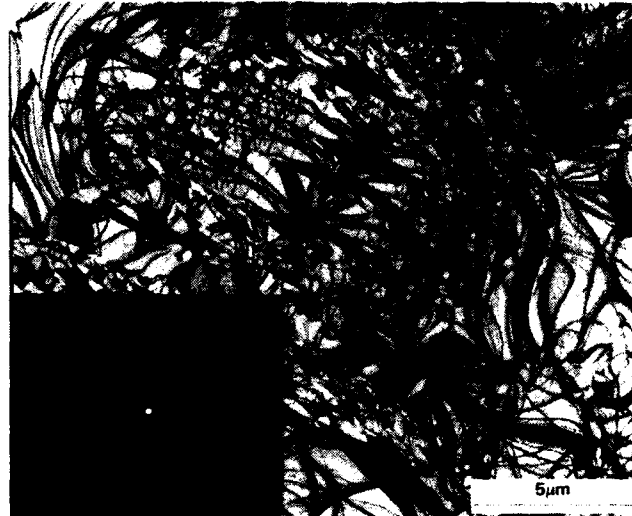


Fig. 4 Fully crystalline 100 nm-thick anatase  $\text{TiO}_2$ , annealed free-standing at  $400^\circ\text{C}$  in Ar for 15 hours.

## 2. PLZT Films

Amorphous films have desirable properties for some optical applications. Stress and impurities in such films are uniformly distributed, and they do not suffer from birefringence and scattering as can large-grain polycrystalline materials. However, for most electrical or electro-optical applications, the optimal properties of a material can only be achieved if it exists in its single-crystal form. Having demonstrated the ability to form amorphous, polycrystalline, and near single-crystal films under different conditions in the  $\text{TiO}_2$  study it was decided to change the emphasis of this research toward the deposition of a more complicated electro-optically active multication film. In such a film any success in creating oriented crystallization could be determined directly through measurements of the dielectric constant. We choose to study lanthanum-modified lead zirconate-titanate (PLZT) because of its importance as an electro-optic material and because a



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significant literature already existed concerning its production by other deposition techniques.

PLZT is a transparent ferroelectric material having an exceptionally strong electro-optic effects. The stoichiometry of this quaternary system,  $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_z)_{1-x/4}\text{O}_3$ , is normally abbreviated as PLZT(x/y/z) where  $y + z = 1$ .

For device applications, PLZT is usually employed in the form of thinned ceramics that require high operating voltages because of their thickness and considerable cost for the microfabrication processing. For these reasons, there has been considerable effort to produce thin film PLZT. This has been done using electron-beam evaporation and rf sputtering where most of the recent work has employed the latter technique.

Although a second-order electro-optic effect has been observed for amorphous thin films, in order to show strong linear electro-optic effects and a high dielectric constant the film must have large perovskite grains (1-2  $\mu\text{m}$ ). This has usually been accomplished by either growing the films on a heated substrate at  $350 < T < 550^\circ\text{C}$  and post annealing to  $650 < T < 800^\circ\text{C}$  or by epitaxially growing the films at  $500 < T < 700^\circ\text{C}$  onto a suitable single-crystal substrate.

Ion-beam deposition is conducted at pressures that are one to two orders of magnitude lower than those needed for rf sputtering so that the depositing particles have considerably higher kinetic energies. One might expect that for a given substrate temperature, ion-beam deposition could produce a higher density film and thus that the subsequent annealing temperature could be reduced.

Ion-beam sputtering is a nonequilibrium deposition technique and the stoichiometry of the films produced may not equal that of the sputtering target. We therefore attempted to study how the film stoichiometry varies with deposition parameters.



PLZT ceramic targets with known stoichiometries were prepared by sol-gel techniques and consolidated by hot isostatic pressing (HIP). Gels of the desired composition were prepared from zirconium isobutylate and titanium isopropoxide mixed with water solutions of lanthanum and lead nitrate. The gels were dehydrated, then fired to 600°C to remove all organics while retaining reactivity in the calcines. These reactive powders were then cold-isostatically pressed into 5 cm-diameter cylindrical green bodies 0.5 cm tall, wrapped in nickel foil and placed in stainless-steel pouches. The HIP containers were heated under vacuum to 400°C and vacuum sealed by welding. Final consolidation was carried out in the HIP furnace at 1200°C and 168 MPa pressure of argon. The ceramics were removed from the HIP containers, and polished to serve as sputtering targets. The sample used in most of this work was made with the stoichiometry  $\text{Pb}_{1.00}\text{La}_{0.085}\text{Zr}_{0.63}\text{Ti}_{0.35}\text{O}_3$ .

The films were grown in the UHV deposition chamber into which a planetary substrate holder and a quartz heat lamp were added (see Fig. 1). Before each growth, the chamber was pumped down to  $<2 \times 10^{-7}$  torr where  $\text{H}_2\text{O}$  remained the primary residual gas. The chamber was then backfilled to  $2 \times 10^{-5}$  torr with oxygen while 5 sccm of argon was flowed through each of the ion guns to bring the total chamber pressure up to  $2 \times 10^{-4}$  torr. With a shield over the substrates, a ceramic PLZT (9/65/35) target was sputter cleaned for 5 minutes with the 1000 eV primary ion beam. Then with the primary ion beam off and the substrate shutter retracted, the substrates were cleaned for 5 minutes with  $\sim 0.1 \text{ mA/cm}^2$  of 500 eV argon ions from the secondary ion gun. The secondary ion gun was then only used during dual ion-beam deposition runs. With a primary ion current of 30 mA, the growth rates were  $\sim 5 \text{ nm/min}$  and the thickness uniformity over the  $4 \text{ cm}^2$  substrates was better than 3%.

The stoichiometries of the deposited films were measured by x-ray photoelectron spectroscopy. For these measurements, peak heights were used and were normalized to the spectrum of the known stoichiometric PLZT ceramic. Each sample was first given a light sputter cleaning for 2 minutes with a





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2.5 keV argon ion beam. A typical spectrum is shown in Figure 5. The relative concentrations of the four metals equalled that of the target to within 10%. When a 50 eV secondary ion-beam was used during the film growth, the concentrations again remained similar. However, with the secondary ion gun operating at 500 eV during dual ion beam deposition or with the planetary tilted so that some of the 1000 eV primary ions were hitting the substrates, the Pb concentration dropped by a factor of five while the ratio of the other three metals remained constant. Heating the substrate to 200°C during growth has no noticeable effect upon the stoichiometry. This ability to produce a near equivalent composition in target and deposited film on the low-temperature substrates was encouraging in that previous workers<sup>7,8</sup> depositing PLZT by diode sputtering have reported the necessity of incorporating excess PbO in their targets in order to achieve proper stoichiometry. The higher substrate temperature employed by these workers (600°C) was probably responsible for the lower sticking coefficient or the reevaporation of Pb from their films. In addition, the formation of a low-temperature deposited amorphous film can significantly increase reactivity and lower transformation temperatures in post-deposition annealing, as was found with the TiO<sub>2</sub> studies.

The index of refraction of our films at 633 nm was measured with a Gaertner auto-gain ellipsometer. Films were grown on Si substrates for these measurements. Indexes of 2.2-2.4 were measured for the single-beam films and 2.1-2.2 for the dual-beam films. Comparing to an index of 2.5-2.6 obtained for epitaxially grown films<sup>9,10</sup> implies that these sputter-grown films are considerably less dense. However, rf-sputtered PLZT (8/65/35) has exhibited an electro-optic effect despite an optical index of 2.1.<sup>11</sup>

The optical transmission spectrum of a 240 nm-thick single ion beam film on fused SiO<sub>2</sub> is shown in Figure 6, where the substrate spectrum has been divided out. Figure 7 shows the optical spectrum of a 340 nm-thick dual-beam film. If the interference effects are accounted for, the dual-beam spectrum is > 95% transparent down to ~ 400 nm while the single beam spectrum shows a loss of transmission throughout the visible. The high energy cut-off of the dual beam film shifts 10 nm toward the uv upon annealing.



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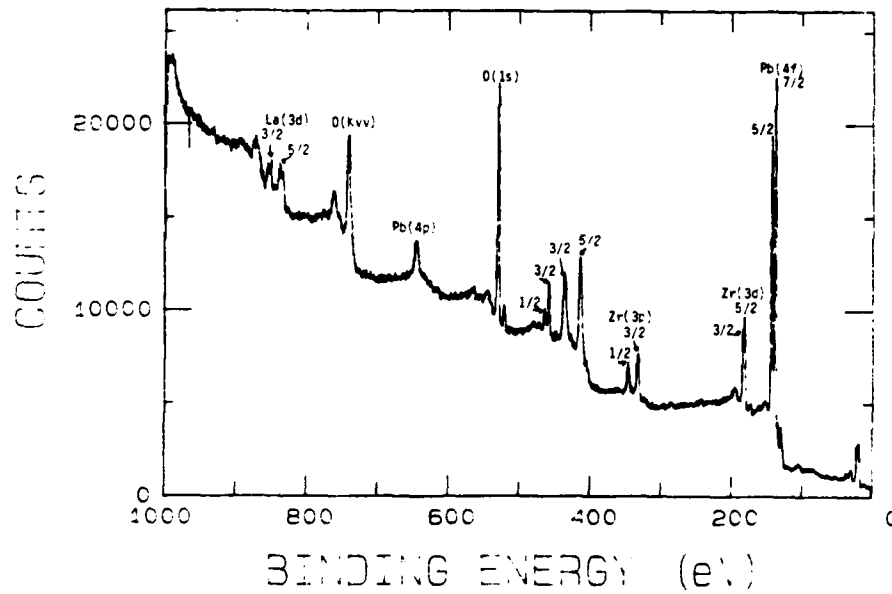


Fig. 5 XPS spectrum of PLZT film taken with Mg  $K_{\alpha}$  radiation.

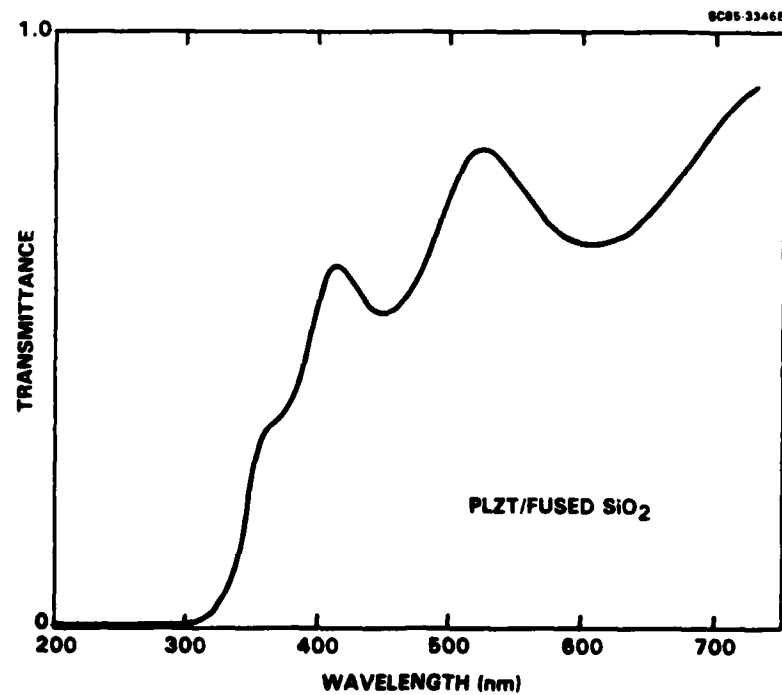


Fig. 6 Transmission spectrum of 240 nm-thick single ion-beam PLZT.



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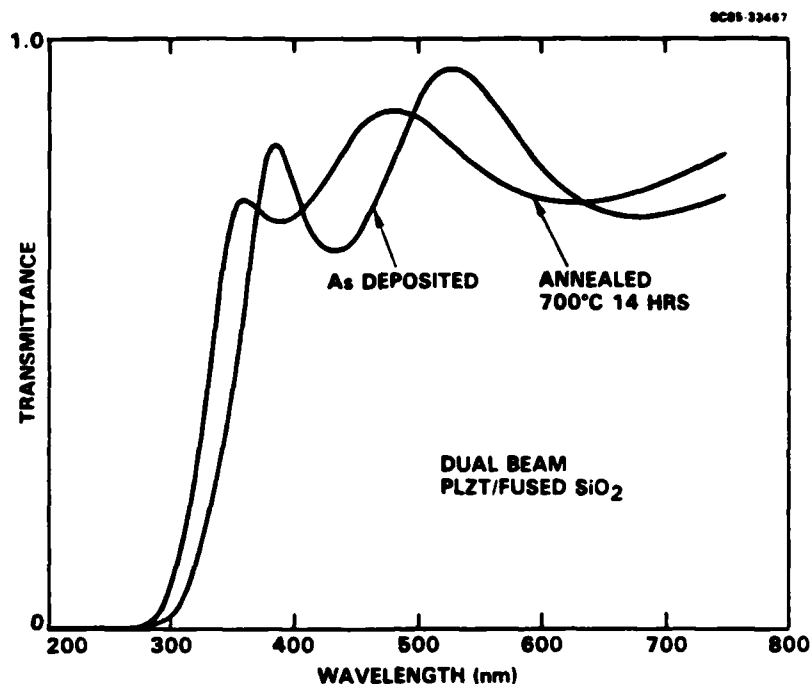


Fig. 7 Transmission spectrum of 340 nm-thick dual-beam PLZT film before and after annealing to 700°C for 14 hours.

As-deposited rf-sputtered films<sup>12</sup> show optical transmission spectra similar to our single ion-beam film. Annealing of the rf-sputtered films improves the transmission so that the spectra then resembles our as-deposited or annealed dual-beam films.

X-ray diffraction measurements of 300 nm-thick single ion-beam films on fused silica substrates showed no structure. When a similar dual ion-beam film (index = 2.2) was annealed at 700°C for 14 h in the presence of PbO powder, one diffraction peak at 30.5° was recorded. This maximum of the peak corresponds to the (110) diffraction peak of Perovskite-type PLZT,<sup>8,12</sup> which is the largest peak in the Perovskite PLZT spectrum, but overlaps the strong 30.0° peak of the cubic pyrochlore form of PLZT. The measured width (1.6° fwhm) corresponds to an average crystallite size of 12 nm. Subsequent annealing of the same film to 800°C for 2 hours had no effect on the spectrum, indicating that some mechanism was preventing grain growth in the films.



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To measure the dielectric constant, a 300 nm-thick film was deposited on a conductive indium tin oxide coated glass substrate. 80 nm of aluminum was then evaporated onto the film through a mask. This created a pattern of 1.0 mm diameter dots. The capacitance of a given dot was then measured at 1 kHz using a HP 4262A digital LCR meter. Dielectric constants for all films were between 25 and 35, even after annealing. This is to be compared with values greater than 1000 previously obtained for perovskite-type PLZT thin films. Low dielectric constants are indicative of either a pyrochlore-type PLZT structure or a multi-phased material.

Transmission electron microscopy (TEM) was used to examine the film microstructure and the film crystallization process. 50 nm-thick films were deposited on freshly cleaved NaCl and KCl substrates, floated off, and mounted on nickel grids for TEM analysis and annealing. The single-beam as-deposited films, produced on a nonrotating substrate, showed a unique electron contrast pattern when observed by TEM. The fully amorphous films had parallel-line contrast patterns, as shown in Figure 8. The spacing of the parallel features are on the order of 12 nm. The large dark spheres are deposits on the surface from the NaCl substrate, while the lighter 1-2 nm spherical shapes are distributed argon-filled porosity in the film.

The contrast patterns in the amorphous PLZT have not been satisfactorily explained, though they can only arise from either a highly regular thickness-density variation or an electro-magnetic interaction of the beam with the film. Since any substrate feature replications or extremely regular thickness-density variations are highly unlikely on this scale, it is quite probable that the contrast variation is associated with the electro-optic properties of the PLZT. The absence of any such contrast variations in dual-beam, rotated, or annealed samples also indicates that the effect is probably associated with short-range molecular ordering occurring only in the nonrotated single-beam film. This phenomena is quite interesting, and will be investigated further.



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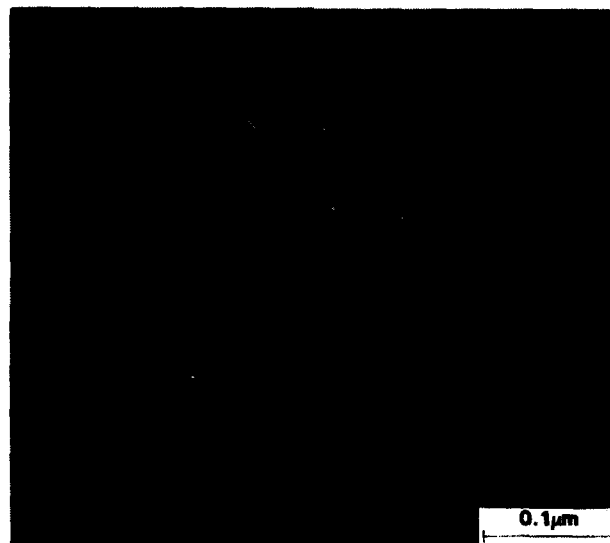


Fig. 8 TEM micrograph of nonrotated, unannealed PLZT film.

Annealing of the free-standing PLZT films at 700°C produced full transformation to a polycrystalline state. The crystalline material shown in Figure 9 has an electron diffraction pattern consistent with a pyrochlore cubic structure in which only the (111), (200), (220), and (113) reflections appear as rings. This diffraction evidence is still not sufficient, however, to distinguish between the cubic, tetragonal, and rhombohedral forms of PLZT, which are possible for the 8-12/65/35 composition, as all have near cubic symmetry and similar cell volumes.<sup>13,14</sup>

Hence, further annealing was carried out, heating a dual ion-beam deposited PLZT film to 700°C and a single ion-beam film to 800°C. Both of these films showed limited grain growth with the appearance of well-formed 0.1  $\mu\text{m}$  rectangular crystallites (see Fig. 10). The diffraction pattern shows the bright spots of the larger grains to generally coincide with the ring patterns of the smaller grain structure, however, several new reflections are apparent, and are consistent with a perovskite structure.



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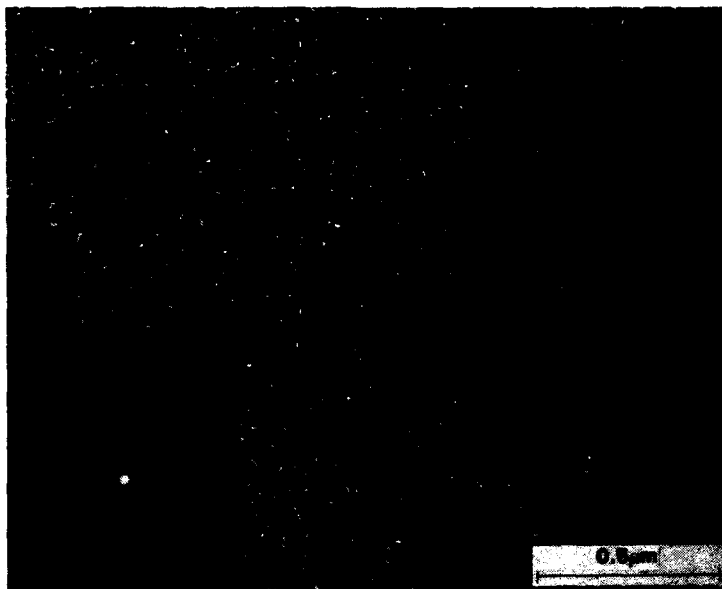


Fig. 9 TEM micrograph of free-standing PLZT film that has been annealed at 700°C for 15 hours.

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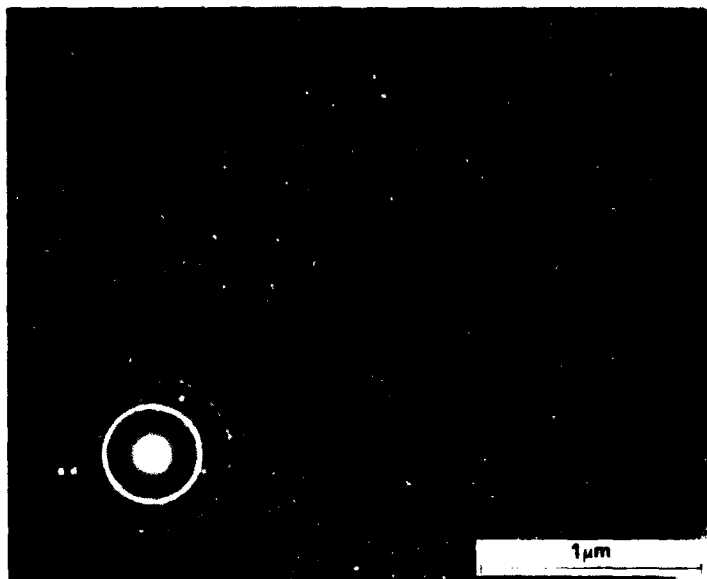


Fig. 10 TEM micrograph of free-standing, single ion-beam PLZT film that has been annealed to 800°C for 2 hours.



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This indicates that temperatures in excess of 800°C are required to convert the nonferroelectric cubic crystalline structure to the ferroelectric perovskite structure in the low-temperature deposited films. This is more than a 150°C higher firing temperature than has been required for PLZT films deposited at substrate temperatures between 450 and 500°C.<sup>9</sup>

The growth of the PLZT grains and this transition to perovskite structure is clearly being restricted by the continuous porosity resulting from the density changes in the film during transformation. This is a result of the argon-filled voids produced during deposition on the unheated substrates. This effect occurred in both the dual-beam and single-beam deposited films, though the extra energy in the dual-beam deposition did produce greater local densities, as reflected by the lower temperature needed for PLZT grain growth. This demonstrates that adequate density is being reached in the solid portions of the film during low-temperature deposition, but that the entrapped argon produces voids which become interconnected porosity during annealing.

The reactive ion-beam technique provides enough surface mobility in the deposition process to produce locally dense multication films with good stoichiometric control, but the problem of inert-gas void inclusion limits the useful applications with low-temperature substrates. These void inclusions could perhaps be minimized by using a more reactive gas, such as O<sub>2</sub> in the primary sputter beam, but again substrate heating provides the simplest approach to avoiding this artifact.

Future efforts in this area will emphasize the use of various sputtering gases and a temperature variation study to determine if void-free films can be formed and still retain the desired amorphous structure.



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#### FUTURE EFFORTS

Future work at the Science Center in this area will be continuing under internal support with the efforts emphasizing the use of reactive-ion and fast-atom beam techniques for the production of well defined stoichiometries and crystalline structures in optical and electro-optical materials.





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#### WRITTEN PUBLICATIONS

F.W. Wodarczyk, D.R. Strauss and A.B. Harker, "Comparison of Optical Coatings Deposited by Novel Physical and Chemical Techniques," in Laser-Induced Damage in Optical Materials: 1983, H.E. Bennett, A.H. Guenther, D. Milam, and B.E. Newman, eds., NBS special publication (in press).

#### PAPERS PRESENTED

"Comparison of Optical Coatings Deposited by Novel Physical and Chemical Techniques," 15th Ann. Symp. on Optical Materials for High Power Lasers, Nov. 14-16, 1983, Boulder, CO.



## PERSONNEL

Alan B. Harker: Group Manager, Member Technical Staff, Applied Spectroscopy Group. Dr. Harker has been at the Science Center since 1973 after receiving his B.A. in Chemistry from Oberlin College, 1968, his Ph.D. in Physical Chemistry from the University of California at Berkeley in 1972, and conducting a year of research at the Lawrence Berkeley Laboratories in applying x-ray photoelectron spectroscopy to the study of the interfacial reactions of aerosol particles. During his 12 years at the Science Center, Dr. Harker has carried out research into the kinetics and mechanisms of a number of homogeneous and heterogeneous reaction systems primarily in environmental and energy-related fields, and has been the principal investigator in developing a basic research program in the application of energetic beam techniques to the deposition of dielectric optical thin films. His work has lead to the development of an extensive spectroscopic and microscopic capability in the Applied Spectroscopy Group, emphasizing the use of surface and microprobe techniques to determine the details of interfacial reactions. Between 1974 and 1979 the primary focus of his work was the heterogeneous reactions of atmospheric aerosols both in the stratosphere and troposphere, which lead to his being selected to the FAA overview panel for determining research needs in upper atmospheric pollution in 1978 (FAA-HAPP). Since 1978 he has been co-principal investigator in and program manager of the Science Center activities in the development and characterization of ceramic and glass nuclear waste forms and the characterization of their interactions with aqueous environments. These activities included 3 years of participation in the DoE-sponsored Alternate Waste Form Program, developing polyphase ceramics as an advanced nuclear waste form, and 3 years of investigating interfacial surface reactions in the DoE High-Level Nuclear Waste Form Leaching Mechanisms Program. During the past four years, Dr. Harker has headed a team of researchers developing energetic-fast atom and ion-beam techniques for depositing dense amorphous films of optical dielectric materials. These studies have recently been extended to the study of surface modification techniques for the toughening of ceramic infrared optical mater-



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ials. Dr. Harker is a member of Sigma Xi, the American Ceramic Society, the American Chemical Society and the Materials Research Society. He has been recognized for his contributions to the field of nuclear waste research by having been nominated 3 times as a co-author for the Best Paper Award in the American Ceramic Society Nuclear Division, receiving the award in 1981, and being selected as Rockwell Engineer of the Year in 1982. Dr Harker has authored and co-authored over 40 technical publications and 3 patents.

F.J. Wodarczyk: Former Member of Technical Staff, Applied Spectroscopy Department, Illinois Institute of Technology, 1966; Ph.D., Harvard University, 1971. Dr. Wodarczyk's background and experience range from molecular spectroscopy and dynamics to laser physics and surface analysis. Doctoral work in microwave spectroscopy under Prof. E. Bright Wilson involved in part the development of a radio frequency-microwave double resonance technique for aiding the analysis of complex spectra. Post-doctoral work at the University of California, Berkeley, with Prof. C. Bradley Moore, dealt with problems in energy transfer and reaction kinetics. Subsequent research at the Air Force Cambridge Research Laboratories involved additional studies of electronic-to-vibrational energy transfer as well as work on optically pumped laser systems. Dr. Wodarczyk joined the Science Center staff in 1978 and has worked on chemical laser systems and novel thin-film deposition techniques, including laser-induced deposition of atomic and molecular films, reactive energetic beam deposition, and the generation of metal oxide films from the photochemical deposition of organo-metallic vapors. In his three years with the Applied Spectroscopy Group, Dr. Wodarczyk has been the principal investigator on a basic study of the nonequilibrium chemistry involved in laser-induced adsorption and desorption of metals and organic vapors sponsored by AFOSR and has been a coinvestigator in the Science Center's internal Optical Thin Film Research program. Dr. Wodarczyk has contributed to 17 technical publications.

P.H. Kobrin: Member of Technical Staff, Applied Spectroscopy Department. B.A., University of California, San Diego, 1978; Ph.D., University of California, Berkeley, 1983. Dr. Kobrin's graduate research under the direc-



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tion of Prof. D.A. Shirley, involved the study of relativistic and many-electron interactions on the photoionization of gases. These effects were studied using continuously tunable synchrotron radiation and time-of-flight photoelectron spectroscopy. His post-doctoral work under Prof. N. Winograd was based on the application of multiphoton resonance ionization to the study of neutral species ejected from ion-bombarded surfaces. Dr. Kobrin joined the Science Center in November, 1984. He has co-authored over 20 scientific publications.

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